# Synthesis, Spectroscopy and Magnetism of Transition-metal Complexes with Pyridylmethylphosphonate Ligands†

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The compounds $[ML_2(H_2O)_2]X_2$ [M = Co, Ni or Cu; L = diethyl 4-pyridylmethylphosphonate (4-pmpe) or diethyl 2-pyridylmethylphosphonate (2-pmpe); X = $NO_3$ or $ClO_4$] have been prepared. Two types of complexes, $[M(4\text{-pmpe})_2(H_2O)_2]X_2$ with the *N*-bonded monodentate ligand and $[M(2\text{-pmpe})_2(H_2O)_2]X_2$ where 2-pmpe acts as a didentate *N,O*-bonded chelate ligand, were obtained. The complexes of $Co^{II}$ and $Ni^{II}$ are isomorphous. The new complexes were identified and characterized by elemental analysis, magnetic measurements and by infrared, electronic and some $^1H$ NMR spectral studies. The crystal and molecular structure of $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$ has been determined: space group $P\bar{1}$, $a = 8.159(1)$, $b = 9.860(1)$, $c = 11.262(1)$ Å, $\alpha = 78.44(1)$, $\beta = 75.11(1)$, $\gamma = 84.30(1)°$, $Z = 2$, $R = 0.0485$, $R' = 0.0445$, for 3078 reflections. The cobalt ion is octahedrally surrounded by two pyridine nitrogens with distances 2.133(3) Å and two oxygens of the phosphoryl groups from two organic ligands at distances of 2.100(2) Å. Two water molecules occupy the fifth and the sixth co-ordination sites *trans* with Co–O bond distances of 2.101(2) Å. The ligand bridges the cobalt ions, thereby forming infinite chains (Co ··· Co 8.159 Å). The spectroscopic and magnetic data are consistent with an octahedral geometry for all the studied complexes, *e.g.* mono- and poly-nuclear for the 2- and 4-pmpe ligands, respectively.

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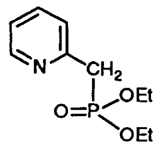
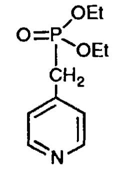
During the past two decades a significant interest in the co-ordination chemistry of phosphonic acids and their esters of pyridine and quinoline has developed; these compounds might be considered to be analogues of naturally occurring phosphates. The ligands are of considerable interest because of their occurrence in numerous organisms [1–8] and their biological activity which is mainly displayed through their ability to inhibit various metalloenzymes, metabolic regulation or perturbation. Hence the investigation of their interaction with various metal ions may contribute to a better understanding of their biological activity. With this purpose the ligands diethyl 2-pyridylmethylphosphonate (2-pmpe) and diethyl 4-pyridylmethylphosphonate (4-pmpe), were synthesised and their co-ordination chemistry towards divalent transition metals was investigated. The 2-pmpe combined a phosphoryl group and a pyridine ring in a conformation which would allow chelation to one metal ion, thus yielding potentially a didentate ligand. The 4-pmpe ligand also combines the pyridine ring and phosphoryl group, but in a sterically unfavourable position to form a chelate. The possibilities of forming polymeric compounds with both ligand ends co-ordinating to a different metal ion or of only one ligand and bonding exists.

In attempts to find the most suitable ligands which may be applied to transport radioisotopes into different parts of the human body we have investigated a larger series of aminophosphonic acids, *i.e.* 2-pyridylmethylphosphonic acid ($2\text{-}H_2pmpa$), 3-pyridylmethylphosphonic acid ($3\text{-}H_2pmpa$), 4-pyridylmethylphosphonic acid ($4\text{-}H_2pmpa$), 2-quinolylmethylphosphonic acid ($2\text{-}H_2qmpa$) as well as their diethyl esters 2-, 3-, 4-pmpe and 2-qmpe.[9,10] These compounds form complexes with transition metals. In particular, it is expected that they form complexes with technetium. Technetium-99m is radioactive which results in very serious problems in X-ray analysis of crystals containing technetium. A detailed knowledge of ligand geometry seems to be very important in predicting the properties of complexes which these ligands form with, *e.g.* technetium.



2-pmpe



4-pmpe

In the present work the synthesis and spectroscopic properties of co-ordination compounds of the ligands 2-pmpe and 4-pmpe with several transition-metal ions and various anions is described. To investigate the binding in detail and to elucidate the detailed nature of the ligand co-ordination a crystal structure of a representative compound, *viz.* $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$, has been determined. Later studies will deal with the other ligands.

## Experimental

*Starting Materials.*—The synthesis of the ligands 2-pmpe and 4-pmpe has been described in detail elsewhere.[9] NMR: 4-pmpe,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

*Non-SI units employed:* Oe = $10^3$ A $m^{-1}$.

**Table 1** Crystal data, experimental and refinement details for $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$

| | |
|---|---|
| Molecular formula | $C_{20}H_{40}Cl_2CoN_2O_{18}P_2$ |
| *M* | 788.32/2 (symmetry centre) |
| Space group | $P\bar{1}$ |
| *a*/Å | 8.159(1) |
| *b*/Å | 9.860(1) |
| *c*/Å | 11.262(1) |
| α/° | 78.44(1) |
| β/° | 75.11(1) |
| γ/° | 84.30(1) |
| $U$/Å$^3$ | 856.7(2) |
| Z | 2 |
| $D_c$/Mg m$^{-3}$ | 1.528 |
| $D_m$/Mg m$^{-3}$ | 1.52 |
| μ(Cu-Kα)/cm$^{-1}$ | 71.5 |
| Radiation | Cu-Kα (λ = 1.541 78 Å) |
| Number of reflections for least-squares fitting | 25 |
| θ range/° | $14 < \theta < 29$ |
| Scan mode | θ–2θ |
| Range of indices and θ/° | *h* −9 to 9, *k* −11 to 12, *l* 0–14; 1–75 |
| *F*(000) | 409 |
| Unique data measured | 3184 |
| Reflections observed $[F_o > 4\sigma(F_o)]$ | 3078 |
| *R*, *R′* | 0.0485, 0.0445 |
| *w* | $1/\sigma^2(F_o)$ |
| Fourier differences (minimum, maximum)/e Å$^{-3}$ | −0.31, 0.25 |
| Maximum shift/error | 0.025 for non-H, 0.5 for H atoms |

**Table 2** Non-hydrogen fractional atomic coordinates (×10$^4$) with estimated standard deviations (e.s.d.s) in parentheses for $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Co | 5 000(0) | 5 000(0) | 5 000(0) |
| Cl | 1 744(1) | 9 509(1) | 2 898(1) |
| P | −2 170(1) | 4 754(1) | 2 076(1) |
| O(1) | −3 125(3) | 4 922(2) | 3 339(2) |
| O(2) | −3 146(3) | 4 097(2) | 1 313(2) |
| O(3) | −1 635(3) | 6 120(2) | 1 182(2) |
| O(4) | 4 787(3) | 7 170(2) | 4 510(3) |
| O(5) | 3 206(6) | 10 740(4) | 5 575(6) |
| N | 3 038(3) | 4 842(2) | 4 103(2) |
| C(1) | 3 078(4) | 5 474(4) | 2 924(3) |
| C(2) | 2 031(4) | 5 163(4) | 2 240(3) |
| C(3) | 853(4) | 4 160(3) | 2 787(3) |
| C(4) | 764(4) | 3 556(3) | 4 013(3) |
| C(5) | 1 836(4) | 3 928(3) | 4 628(3) |
| C(6) | −220(4) | 3 711(4) | 2 056(3) |
| C(7) | −3 990(6) | 2 795(5) | 1 841(4) |
| C(8) | −4 423(14) | 2 354(10) | 769(6) |
| C(9) | −2 199(14) | 7 462(4) | 1 455(7) |
| C(10) | −1 369(16) | 8 626(7) | 524(9) |
| O(6) | 1 912(5) | 8 730(5) | 4 026(4) |
| O(7) | 2 794(7) | 9 012(4) | 1 880(4) |
| O(8) | 2 142(10) | 10 826(4) | 2 882(6) |
| O(9) | 109(7) | 9 734(11) | 2 814(7) |

**Table 3** Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$

| | | | |
|---|---|---|---|
| Co–O(1) | 2.100(2) | O(2)–C(7) | 1.461(5) |
| Co–O(4) | 2.101(2) | O(3)–C(9) | 1.424(5) |
| Co–N | 2.133(3) | N–C(1) | 1.343(4) |
| Cl–O(6) | 1.378(4) | N–C(5) | 1.337(4) |
| Cl–O(7) | 1.388(4) | C(1)–C(2) | 1.379(6) |
| Cl–O(8) | 1.351(5) | C(2)–C(3) | 1.386(5) |
| Cl–O(9) | 1.355(6) | C(3)–C(4) | 1.376(5) |
| P–O(1) | 1.469(2) | C(3)–C(6) | 1.495(6) |
| P–O(2) | 1.571(3) | C(4)–C(5) | 1.362(5) |
| P–O(3) | 1.538(2) | C(7)–C(8) | 1.494(11) |
| P–C(6) | 1.804(3) | C(9)–C(10) | 1.477(10) |

| | | | |
|---|---|---|---|
| O(1)–Co–O(4) | 90.0(1) | P–O(2)–C(7) | 121.2(2) |
| O(1)–Co–N | 91.4(1) | P–O(3)–C(9) | 124.4(4) |
| O(4)–Co–N | 89.7(1) | Co–N–C(1) | 122.7(2) |
| O(6)–Cl–O(7) | 112.9(3) | Co–N–C(5) | 120.5(2) |
| O(6)–Cl–O(8) | 109.5(3) | C(1)–N–C(5) | 116.1(3) |
| O(6)–Cl–O(9) | 113.2(4) | N–C(1)–C(2) | 123.4(3) |
| O(7)–Cl–O(8) | 107.7(3) | C(1)–C(2)–C(3) | 119.2(3) |
| O(7)–Cl–O(9) | 112.8(4) | C(2)–C(3)–C(4) | 117.3(3) |
| O(8)–Cl–O(9) | 99.7(5) | C(2)–C(3)–C(6) | 121.2(3) |
| O(1)–P–O(2) | 115.8(1) | C(4)–C(3)–C(6) | 121.5(3) |
| O(1)–P–O(3) | 114.4(1) | C(3)–C(4)–C(5) | 120.0(3) |
| O(1)–P–C(6) | 113.2(2) | N–C(5)–C(4) | 123.9(3) |
| O(2)–P–O(3) | 101.5(1) | P–C(6)–C(3) | 113.1(2) |
| O(2)–P–C(6) | 105.7(1) | O(2)–C(7)–C(8) | 105.3(5) |
| O(3)–P–C(6) | 104.9(2) | O(3)–C(9)–C(10) | 115.1(7) |

$^1$H ($CCl_4$), δ 1.23 (t, 6 H, $^3J_{HH}$ = 6.0, $2POCH_2CH_3$), 3.18 (d, 2 H, $^2J_{PCH}$ = 22.0, $CH_2P$), 3.92 (dq, 4 H, $^3J_{POCH}$ = 6.0, $^3J_{HH}$ = 6.0, $2POCH_2CH_3$), 7.1–7.3 (m, 2 H, aryl H on C$^3$ and C$^5$) and 8.4 (d, 2 H, $^3J_{HH}$ = 6.0, aryl H on C$^2$ and C$^6$); $^{31}$P ($CHCl_3$), δ 23.66; 2-pmpe, $^1$H ($CCl_4$), δ 1.23 (t, 6 H, $^3J_{HH}$ = 6.0, $2POCH_2CH_3$), 3.42 (d, 2 H, $^2J_{PCH}$ = 22.0, $CH_2P$), 4.09 (dq, 4 H, $^3J_{POCH}$ = 7.0, $^3J_{HH}$ = 7.0, $2POCH_2CH_3$), 6.97–7.80 (m, 3 H, aryl H) and 8.42 (d, 1 H, $^3J_{HH}$ = 5.0 Hz, aryl H on C$^6$); $^{31}$P ($CHCl_3$), δ 24.49.

The co-ordination compounds were prepared by dissolving the appropriate hydrated metal perchlorate or nitrate (1 mmol) in hot ethanol (10 cm$^3$) and tetrahydrofuran (thf, 5 cm$^3$) and adding to a solution of the ligand (2 mmol) in hot ethanol 15 cm$^3$). After filtration of the hot reaction mixture, to remove any impurities, the complexes crystallized on cooling. In some cases, however, evaporation of part of the solvent was necessary before crystallization would occur.

**CAUTION**: The compounds described contain perchlorate anions. Although no accidents occurred during the present experimental work it should be pointed out that the use of perchlorates is hazardous because of their potential explosive nature. Perchlorates should only be prepared in small amounts and should be handled with care.

Metal analyses were carried out complexometrically with ethylenediaminetetraacetate (edta) as the complexing agent.[11]

*Physical Methods*.—Infrared spectra (50–4000 cm$^{-1}$) were recorded on a Perkin Elmer 180 spectrophotometer using KBr pellets, solid-state electronic spectra (28 000–50 000 cm$^{-1}$) on a Beckman UV 5240 spectrophotometer fitted with a reflectance attachment, using MgO as a reference. Electron spin resonance spectra of powdered compounds were obtained with a Radiopan SE/X 2543 spectrophotometer at X-band frequencies at room temperature and at 77 K (liquid nitrogen). Solid diphenylpicrylhydrazyl (dpph) was used as the reference and magnetic field was calibrated with proton and lithium NMR probes. Proton nuclear magnetic resonance spectra were recorded on a Varian EM 360 spectrophotometer employing a frequency of 60 MHz with $SiMe_4$ as internal standard.

Magnetic susceptibility measurements (80–300 K) were carried out using the Gouy method on a sensitive Cahn RM-2 electronic balance at a magnetic field strength 9.9 kOe. Over the temperature range 4.2–300 K measurements were made by the Faraday method, using a Cahn RG-HV electrobalance and a magnetic field of 5.25 kOe. The calibrant employed was $HgCo(NCS)_4$, for which the magnetic susceptibility was taken as $16.44 \times 10^{-6}$ cm$^3$ g$^{-1}$.[12] Corrections for diamagnetism of the constituent atoms were made by use of Pascal constants.[13] The effective magnetic moments were calculated from $\mu_{eff} = 2.83\,(\chi_M T)^{\frac{1}{2}}$ using temperature-independent paramagnetism of $60 \times 10^{-6}$ (Cu$^{II}$) and $220 \times 10^{-6}$ cm$^3$ mol$^{-1}$ (Ni$^{II}$).

**Table 4** Analytical data for the complexes with calculated values in parentheses

| Complex | Analysis (%) M | H | C | N | M.p./ °C |
|---|---|---|---|---|---|
| $[Co(2\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 7.95 | 4.65 | 31.65 | 3.60 | 211–213 |
|  | (7.85) | (4.80) | (31.90) | (3.70) |  |
| $[Co(2\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 8.70 | 5.45 | 35.55 | 8.25 | 114–116 |
|  | (8.70) | (5.35) | (35.45) | (8.25) |  |
| $[Ni(2\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 7.80 | 4.75 | 31.55 | 3.55 | 221–224 |
|  | (7.80) | (4.80) | (31.95) | (3.70) |  |
| $[Ni(2\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 8.60 | 5.25 | 35.45 | 8.35 | 90–99 |
|  | (8.65) | (5.35) | (35.45) | (8.25) |  |
| $[Cu(2\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 8.45 | 4.45 | 31.90 | 3.80 | 209–212 |
|  | (8.40) | (4.80) | (31.75) | (3.70) |  |
| $[Cu(2\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 9.40 | 5.40 | 35.65 | 8.30 | 216–218 |
|  | (9.30) | (5.30) | (35.20) | (8.20) |  |
| $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 7.80 | 4.70 | 31.50 | 3.50 | 208–209 |
|  | (7.85) | (4.80) | (36.90) | (3.70) |  |
| $[Co(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 8.70 | 5.50 | 35.60 | 8.35 | 147–150 |
|  | (8.70) | (5.35) | (35.45) | (8.70) |  |
| $[Ni(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 7.60 | 4.60 | 31.75 | 3.60 | 221–223 |
|  | (7.80) | (4.80) | (31.95) | (3.70) |  |
| $[Ni(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 8.75 | 5.60 | 35.80 | 8.45 | 145–150 |
|  | (8.65) | (5.35) | (35.45) | (8.25) |  |
| $[Cu(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 8.45 | 4.85 | 31.05 | 3.90 | 203–206 |
|  | (8.40) | (4.80) | (31.75) | (3.70) |  |
| $[Cu(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 9.10 | 5.40 | 35.10 | 8.30 | 141–144 |
|  | (9.30) | (5.30) | (35.20) | (8.20) |  |

*Crystallography.*—Crystals of $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2{\cdot}2H_2O$ were grown from ethanol solution; a rather irregularly shaped crystal (*ca.* 0.2 × 0.3 × 0.5 mm) was used for the data collection on a CAD-4 automated single-crystal diffractometer. Experimental details are given in Table 1.

The structure was solved using heavy-atom methods and refined by least-squares methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found from Fourier-difference syntheses and refined isotropically.

All calculations were performed using SHELX 76, SHELX 86[14,15] and CSU.[16] Structure plots were made with PLUTO.[17] Final atomic coordinates are given in Table 2, bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

Analytical data for the co-ordination compounds of general formula $[M(2\text{-pmpe})_2(H_2O)_2]X_2$ and $[M(4\text{-pmpe})_2(H_2O)_2]X_2$, ($M = Co^{II}$, $Ni^{II}$ or $Cu^{II}$; $X = NO_3^-$ or $ClO_4^-$) are given in Table 4. The characteristic vibrations of the anions $ClO_4^-$ were easy to recognise in the IR spectra. All 4-pmpe complexes have very similar IR spectra from which it can be concluded that they must have very similar structures. The differences in their X-ray powder diffraction patterns, however, indicate different crystal lattices.

The NMR signals of the zinc(II) co-ordination compounds are slightly shifted when compared with those of the free ligand. This indicates that in dimethyl sulfoxide solution they do not dissociate. It is also evident from the spectra that the ligand has not decomposed.

*Spectroscopy.*—The ligand-field spectra of the investigated complexes (Table 5) are typical for six-co-ordinate $Co^{II}$ and $Ni^{II}$ in octahedral environments. The rather high values of the ligand-field Racah parameter $B$ may suggest a distorted-octahedral geometry;[19,20] the crystal-field parameters $B$ and $Dq$ were calculated using well known methods.[18,20]

The electronic spectra of the cobalt(II) complexes are typical of high-spin, six co-ordinated, weakly tetragonally distorted $Co^{II}$. The Tanabe–Sugano diagram in $O_h$ symmetry shows three bands, corresponding to ${}^4T_{1g} \longrightarrow {}^4T_{2g}(\nu_1)$, ${}^4T_{1g} \longrightarrow {}^4A_{2g}(\nu_2)$ and ${}^4T_{1g} \longrightarrow {}^4T_{2g}(P)(\nu_3)$ transitions. The band at *ca.* 20 000 cm$^{-1}$ was assigned to the $\nu_3$ transition. This band is not split in tetragonal symmetry. Its asymmetric outline in the higher-energy region (shoulder at *ca.* 21 000 cm$^{-1}$) has been assigned to spin–orbit components and to spin-forbidden transitions. The band at *ca.* 8000 cm$^{-1}$ corresponds to the $\nu_1$ transition in $O_h$ symmetry. In tetragonal symmetry it may undergo splitting into at least two components. For the present complexes no splitting is observed, but rather an asymmetric band shape, which may suggest tetragonal distortion. At ≈16 000–17 000 cm$^{-1}$ the weak shoulder, most likely originating from the $\nu_2$ transition is observed ($\nu_2$ is usually not observed, or is a very weak band).[18]

The electronic spectra of the nickel(II) complexes are characteristic of six-co-ordinated, weakly tetragonally distorted $Ni^{II}$. Three spin-allowed bands, corresponding to the ${}^3A_{2g} \longrightarrow {}^3T_{2g}(P)(\nu_1)$, ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)(\nu_3)$ transitions in $O_h$ symmetry are observed at *ca.* 9000, in the range 15 100–16 200 and in the range 25 300–26 700 cm$^{-1}$, respectively. In the electronic spectra of high-spin tetragonal nickel(II) complexes usually no splitting of the $\nu_3$ band is observed, but a clear splitting of $\nu_1$ and $\nu_2$ often occurs. For the present complexes no splitting of $\nu_1$ occurred; however, the shoulder at *ca.* 13 500 cm$^{-1}$ could also originate from a splitting of the $\nu_2$ band,[19] in addition to spin–orbit splitting and admixture with a singlet.[20]

The copper(II) complexes exhibit one asymmetric band in the visible spectrum at 14 000–15 000 cm$^{-1}$, associated with the ${}^2E_g \longrightarrow {}^2T_{1g}$ transition in $O_h$ symmetry.

The compounds $[M(2\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ ($M = Co^{II}$ or $Ni^{II}$) are isomorphous as deduced from their infrared spectra and X-ray powder patterns, *i.e.* the band positions, intensities and relative shapes are very much the same.

Evidence for the presence of $ClO_4^-$ and $NO_3^-$ was supplied by the infrared spectra. Strong absorption bands of the nitrate group in the region of 1385 and 800 cm$^{-1}$ are observed, as well as a strong, broad absorption band around 1100 and a sharp band at 620 cm$^{-1}$ characteristic of ionic $ClO_4^-$.[21] In the infrared spectrum of the ligand a strong band at 1250 cm$^{-1}$ is observed which is assigned to the P=O group. In the spectra of the

**Table 5** Electronic spectral data for $[M(2\text{-pmpe})_2(H_2O)_2]X_2$ and $[M(4\text{-pmpe})_2(H_2O)_2]X_2$[a] complexes and EPR parameters of copper compounds

| Compound | Band positions (cm$^{-1}$) | | | $Dq^b$/cm$^{-1}$ | $B^b$/cm$^{-1}$ |
|---|---|---|---|---|---|
| $[Co(2\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 21 040(sh) | 20 000 $\nu_3$ | 8 390 $\nu_1$ | 925 | 855 |
| $[Co(2\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 20 620(sh) | 19 600 $\nu_3$ | 8 470 $\nu_1$ | 940 | 825 |
| $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 21 280(sh) | 20 000 $\nu_3$ | 8 090 $\nu_1$ | 885 | 870 |
| $[Co(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 21 280(sh) | 20 200 $\nu_3$ | 8 710 $\nu_1$ | 965 | 850 |
| $[Ni(2\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 25 510 $\nu_3$ | 15 380 $\nu_2$ | 9 120 $\nu_1$ | 910 | 905 |
| $[Ni(2\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 25 320 $\nu_3$ | 15 110 $\nu_2$ | 8 920 $\nu_1$ | 890 | 880 |
| $[Ni(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 25 640 $\nu_3$ | 15 500 $\nu_2$ | 9 610 $\nu_1$ | 960 | 820 |
| $[Ni(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 26 670 $\nu_3$ | 16 210 $\nu_2$ | 9 730 $\nu_1$ | 975 | 835 |

| | | | Spectroscopic splitting factors | | |
|---|---|---|---|---|---|
| | | $T$/K | $g_\perp$ | $g_\parallel$ | $g_{av}$[c] |
| $[Cu(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 15 870 | r.t.[d] | $2.07_5$ | $2.30_9$ | $2.15_6$ |
| | | 77 | $2.07_5$ | $2.29_4$ | $2.15_0$ |
| $[Cu(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 15 380 | r.t. | $2.05_7$ | $2.18_6$ | $2.10_1$ |
| | | 77 | $2.05_7$ | $2.19_9$ | $2.10_5$ |
| $[Cu(2\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 14 920 | r.t. | $2.07_0$ | $2.31_9$ | $2.15_6$ |
| | | 77 | $2.07_0$ | $2.32_2$ | $2.15_9$ |
| $[Cu(2\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 13 330 | r.t. | $2.09_7$ | $2.21_6$ | $2.13_7$ |
| | | 77 | $2.08_0$ | $2.20_3$ | $2.12_2$ |

[a] X = $ClO_4$ or $NO_3$. [b] Calculated from ref. 18. [c] $g_{av} = [\frac{1}{3}(g_\parallel^2 + 2g_\perp^2)]^{\frac{1}{2}}$. [d] r.t. = Room temperature.

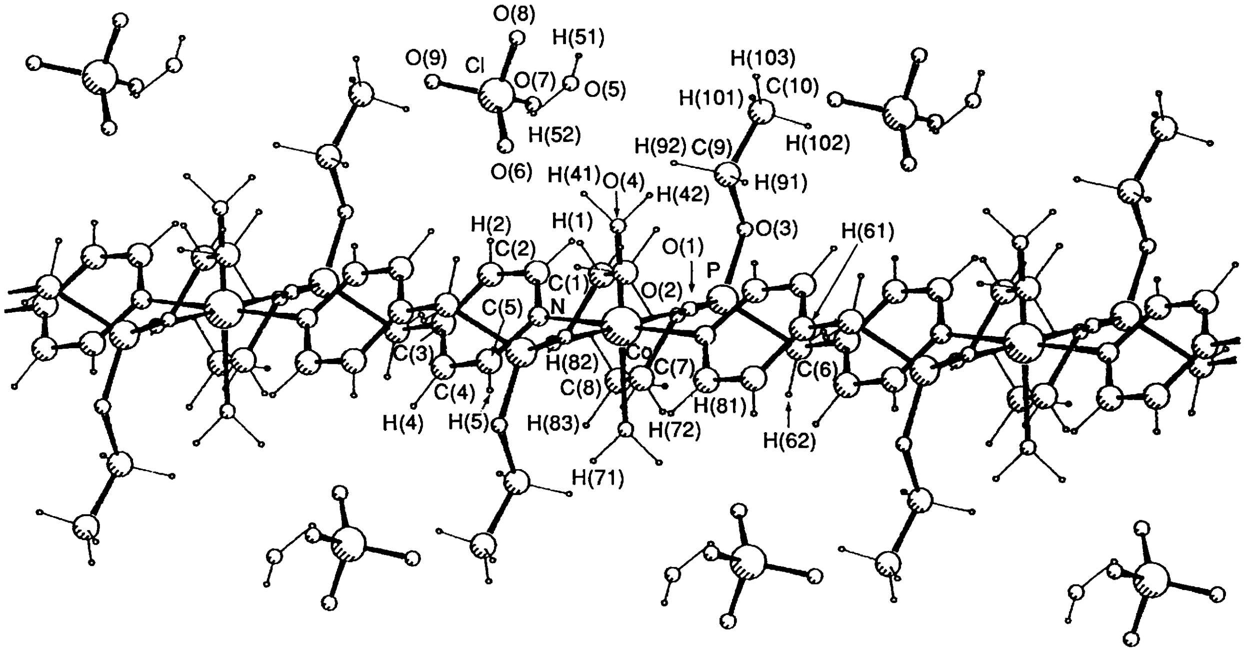

Fig. 1 A PLUTO drawing of $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$ with the atomic labelling used

complexes this band is shifted towards lower wavenumbers with a maximum around 1220 cm$^{-1}$, suggesting co-ordination of the metal ion through the P=O oxygen atom of the ligand.[22–26]

The IR spectra of the perchlorate compounds are very similar in line shapes and relative intensities throughout the series M = Co, Ni or Cu indicating a similar ligand conformation for all the compounds.

The ligand-field parameters of $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$ indicate a distorted-octahedral geometry as confirmed by the X-ray structure analysis.

The stoichiometry of the complexes $[ML_2(H_2O)_2][NO_3]_2$ was established from elemental analyses and metal determinations. This implies a $N_2O_4$ chromophore around the metal ions, where the oxygen can originate either from water molecules or from nitrate ions. The nitrate stretching vibration at 1700 cm$^{-1}$ is not split, indicating ionic (non-bonded) nitrates.[21] The sharp δ(H–O–H) bending of co-ordinated water is observed at 1600–1650 cm$^{-1}$. From the X-ray patterns it can be concluded that there is no isomorphism within the group of nitrates. The ligand-field data for the copper compound are consistent with a $d_{x^2-y^2}$ ground state of the copper ion in an elongated-octahedral geometry.

*The Structure of* $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$.—A single-crystal study of this representative compound was undertaken to elucidate the structure of these compounds and to enable the interpretation of their magnetic properties.

A view of the polymeric chain structure of the complex in the crystal with the atom numbering is shown in Fig. 1. The bond lengths and angles do not deviate significantly from average standard values (Table 3). The compounds crystallizes with two water molecules. The cobalt ion lies at a centre of symmetry and has a six-co-ordinate environment formed by two pyridine nitrogens, two lattice phosphoryl-group oxygens from two organic ligands and two water oxygens. The co-ordination geometry is approximately octahedral with bond lengths from

**Table 6** Magnetic data and computed best-fit parameters for $[M(4\text{-pmpe})_2(H_2O)_2]X_2$ compounds[a]

| Compound | Curie constant,[b] $C$/cm$^3$ mol$^{-1}$ K | Weiss constant,[b] K | Magnetic susceptibility, $10^6\ \chi_M$/cm$^3$ mol$^{-1}$ at r.t. | $\mu_{eff}$ r.t. | $\mu_{eff}$ 4.2 K | Model of magnetic interaction | Parameter | $R$[c] |
|---|---|---|---|---|---|---|---|---|
| $[Cu(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 0.51 | −2.7 | 1 740 | 2.02 | 1.91 | Ising chain[29,30] | $J = -0.3$ cm$^{-1}$<br>$g = 2.31$ | $5.14 \times 10^{-3}$ |
| $[Cu(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 0.50 | −8.9 | 1 700 | 1.9 | 1.82 | Ising chain[29,30] | $J = -0.6$ cm$^{-1}$<br>$g = 2.25$ | $5.47 \times 10^{-2}$ |
| $[Ni(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 1.20 | −7.7 | 4 010 | 3.07 | 2.69 | Ising chain[31] | $J = -0.1$ cm$^{-1}$<br>$g = 2.49$<br>$D = -0.041$ cm$^{-1}$ | $6.14 \times 10^{-2}$ |
| $[Ni(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 1.28 | −13.9 | 4 160 | 3.12 | 2.54 | Ising chain[31] | $J = -0.3$ cm$^{-1}$<br>$g = 2.57$<br>$D = -0.026$ cm$^{-1}$ | $4.46 \times 10^{-2}$ |
| $[Co(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ | 3.14 | −26.0 | 9 890 | 4.81 | 3.66 | | | |
| $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ | 3.54 | −19.0 | 11 200 | 5.14 | 3.78 | | | |

[a] M = Cu$^{II}$ or Ni$^{II}$ and X = $NO_3$ or $ClO_4$. [b] In the temperature range 100 K to r.t. [c] $\Sigma_i\,[(\chi_i^{exptl} - \chi_i^{calc})^2/(\chi_i^{exptl})^2]$.

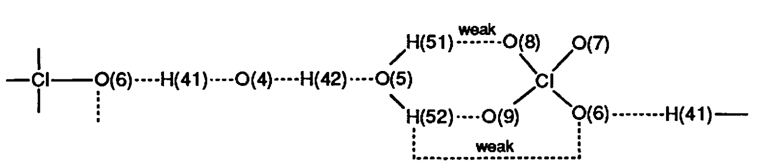

**Fig. 2** Schematic drawing of the hydrogen-bonding pattern in $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$

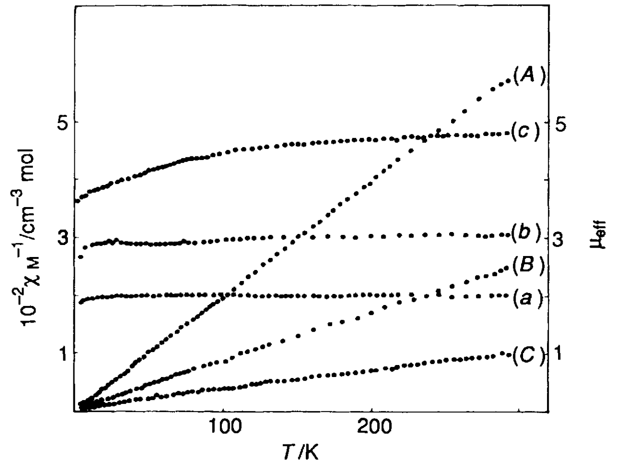

**Fig. 3** Relation of the magnetic moment ($\mu_{eff}$) and reciprocal magnetic susceptibility ($\chi_M^{-1}$) *vs.* $T$ for $[Cu(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ (*A*,*a*), $[Ni(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ (*B*,*b*) and $[Co(4\text{-pmpe})_2(H_2O)_2][NO_3]_2$ (*C*,*c*). Lower case letters refer to $\mu_{eff}$

2.100(2) to 2.133(2) Å and bond angles from 89.7(1) to 90.0(1)°. The Co–N and Co–O bond lengths are characteristic of high-spin cobalt(II).[27,28]

The nitrogen and oxygen O(1) atoms of every ligand molecule are connected in the crystal with two cobalt ions forming infinite polymeric chains. The polymeric chain structure is clearly visible in Fig. 1 (left to right). The Co ··· Co distance is 8.159 Å. The water ligands are axially co-ordinated (vertical). The chains are separated by perchlorate ions and water molecules in the lattice. The bond lengths in the ligand are normal. The crystal packing is determined both by hydrogen bonding and van der Waals interactions. The water molecules which are involved in hydrogen bonds with perchlorate ion oxygens are also connected to each other, as shown in Fig. 2.

*Magnetic Properties.*—The EPR spectra of the copper compounds (Table 5) indicate a tetragonally distorted octahedral co-ordination. The nickel compounds do not exhibit X-band spectra, and the cobalt compounds show no lines at room temperature but one or two lines at 77 K at $g = 6.93$ and 3.66.

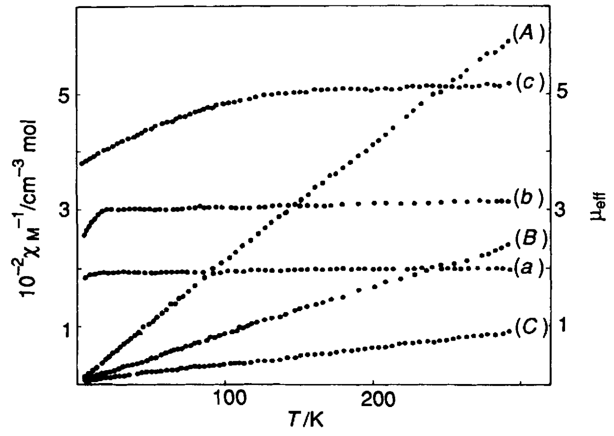

**Fig. 4** Relation of the magnetic moment ($\mu_{eff}$) and reciprocal magnetic susceptibility ($\chi_M^{-1}$) *vs.* $T$ for $[Cu(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ (*A*,*a*), $[Ni(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ (*B*,*b*) and $[Co(4\text{-pmpe})_2(H_2O)_2][ClO_4]_2$ (*C*,*c*). Lower case letters refer to $\mu_{eff}$

Variable-temperature (4.2–300 K) magnetic susceptibility measurements on the $[Co(4\text{-pmpe})_2(H_2O)_2]X_2$ (X = $NO_3$ or $ClO_4$) complexes (Table 6) indicated properties typical of high-spin Co. The nickel(II) and copper(II) complexes with 4-pmpe had a constant value of $\chi_M T$ *versus* temperature. The value of $\chi_M T$ decreased only at the lowest temperatures (Figs. 3 and 4). This suggests the possiblity of at best a very weak magnetic interaction between the paramagnetic centres ($Cu^{2+}$ and $Ni^{2+}$) inside the dibridged linear chain $[M(4\text{-pmpe})_2M]_n$ (see Fig. 1).

Results of computer calculations of the exchange parameters $J$ in the Hamiltonian $\mathscr{H} = -2J\hat{S}_i\cdot\hat{S}_j$, (refs. 29–31) are presented in Table 6. The observed antiferromagnetic coupling is very weak indeed and the metallic centres inside the chain are practically magnetically isolated.

## Conclusion

The results described above have manifested in that the ligand

2-pmpe in co-ordination compounds with $Co^{II}$, $Ni^{II}$ and $Cu^{II}$ acts in a didentate manner through the P=O oxygen atom and the nitrogen atom of the pyridine ring to form complexes involving six-membered chelate rings. The 4-pmpe ligand forms polymeric high-spin six-co-ordinated complexes in which both ends of the ligand co-ordinate to different metal ions, as demonstrated by the crystal structure.

Future studies will deal with the co-ordination chemistry of other metal ions and related ligands, such as 3-pmpe and 2-qmpe.

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